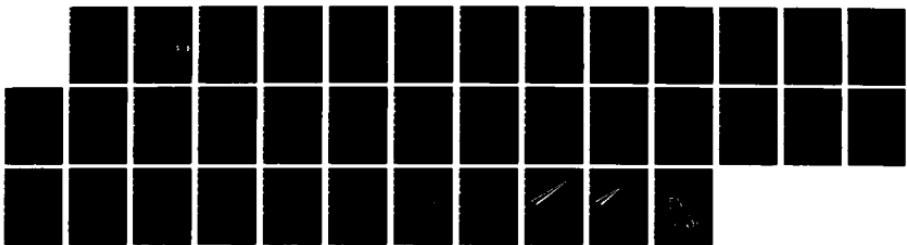
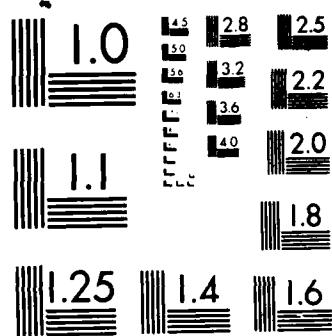


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SOLID PHASE EQUILIBRIA IN THE Au-Ga-As, Au-Ga-Sb, Au-In-As,
AND Au-In-Sb TERNARIES

by

Thomas C. Tsai and R. Stanley Williams

Prepared for Publication

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Solid Phase Equilibria in the Au-Ga-As, Au-Ga-Sb, Au-In-As, and Au-In-Sb Ternaries

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Abstract

The Au-Ga-As, Au-Ga-Sb, Au-In-As, and Au-In-Sb ternaries were surveyed using X-ray powder diffraction to determine which metallic phases exist at equilibrium with the III-V compound semiconductors. In closed, small-volume systems (i.e., formation of gas-phase products was prevented), Au does not react with GaAs but does react with the other III-V's investigated to produce Au - Group III intermetallic compounds and another solid phase containing the group V element. However, each semiconductor formed pseudobinary systems with at least two different intermetallic compounds. The bulk phase diagrams determined in this study provide frameworks within which much of the experimental data in the literature concerning the products of reactions at Au/III-V interfaces can be understood.

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I. Introduction

The study of thin metal films on compound semiconductors has attracted a great deal of attention in the past decade because of the interest in the electronic states that form and the behavior of the resulting Schottky barrier.¹⁻¹⁹ In order to control the electrical properties of these systems, one must first understand the chemistry that occurs at the metal/semiconductor interface. However, despite a large amount of recent work examining the metallurgy of thin films on semiconductors, especially Au on III-V substrates, it is clear that no broad framework yet exists to explain the observations that have been reported. The earliest studies of the Au/III-V interfaces noted that "interdiffusion" of the metal and semiconductor occurred after samples were heated to relatively low temperatures (i.e., 573K or so).²⁻⁶ Later studies recognized that this diffusion was actually the result of a chemical reaction.^{1,7-17} The general pattern that appears from these studies is that heating a Au film / III-V substrate system leads to the decomposition of the semiconductor near the interface and the release of volatile elemental group-V through the grain boundaries of the metal film.⁹ Such behavior can be rationalized, since the Pauling electronegativity of Au is higher than that of the group V elements.²⁰ Thus, Au acts as an oxidizing agent and displaces the less electronegative group V elements in combining with the highly electropositive group III metals. Although such a picture is consistent with experimental observations, it does not have any predictive value.

As Schwartz has shown,²¹⁻²³ a necessary step in understanding the chemistry of thin oxide films on compound semiconductors was the study of the O-III-V ternary phase diagrams. Very little work on bulk Au-III-V phase diagrams has been performed previous to this examination, but the paper of Panish²⁴ on the bulk Au-Ga-As system provides a background for the study of Au films on GaAs. Panish's results indicated that bulk Au and GaAs are not thermodynamically stable with respect to one another, and that the ternary phase diagram was rather complex. Although he did not map the phase diagram in detail, he did determine that both AuGa and AuGa₂ intermetallic compounds formed pseudobinary cuts with GaAs through the ternary phase diagram. This observation is important in that it shows what pure metallic phases are thermodynamically stable with respect to GaAs, since in general the phase rule would predict that there should be three solid phases in equilibrium for a system made up of three elements (in the absence of any constraints other than fixed temperature and pressure).²⁵ The purpose of this work is to extend the studies of Panish²⁴ and to examine the Au-Ga-Sb, Au-In-As, and Au-In-Sb systems along the lines of the phase diagram investigations of Schwartz.²¹⁻²³ The intention is not to map the phase diagrams in great detail, but rather to determine which metallic phases are stable with respect to the III-V compound semiconductors, see if any general pattern may be observed, and use this information to better understand and design thin metal films on compound semiconductor substrates.²⁶

The experimental procedure used in this investigation is described in the next section. The results are presented and discussed in section III, and the final section contains the conclusions of this work.

II. Experimental Procedure

The experiments involved the identification of the stable bulk phases for atomic compositions within the four ternary systems: Au-Ga-As, Au-Ga-Sb, Au-In-As, and Au-In-Sb. Samples were prepared by weighing out the required amounts of the elements (all reagent grade with purity better than 99.99%) and/or semiconductor grade InSb, GaSb or GaAs. The total sample mass was on the order of 1 gram and the estimated error in the atomic compositions of the samples was less than one part in one thousand.

Each sample was placed in a fused silica capsule with inner volume 5 cm³, which was evacuated to about 10⁻⁶ torr and sealed. The sealed capsules were placed in a resistance furnace and heated to above the melting point of each sample (usually about 1273K) for one week, to ensure homogenization of the melt. They were then cooled to either 298K or 873K at a rate of 5-10 Kelvin per hour (slower near the melting point of a phase that solidified). The 873K samples were quenched by dropping them into ice water. The cooling procedures usually required one week, and the resulting samples were solid lumps with perhaps some powder clinging to the walls of the capsule.

After removing the samples from the capsules, they were examined using a microscope. Sometimes a clear boundary separating phases was evident, but usually the samples were mixtures of small crystallites of the different phases. Filings were removed from two sides of each sample, and all of the samples were cut in half to obtain filings from the center. These filings were examined with a Phillips X-ray powder diffractometer, which was interfaced to a microcomputer that controlled the scan rate and

collected the data digitally, to determine the reaction products. The diffraction data was collected at 0.1° intervals, with a counting time of 10 seconds at each angle; the total time required for a complete scan (2θ from 10 to 100 degrees) was three hours and the typical signal-to-noise ratio for a strong diffraction peak was 40 to 1. The composition of each sample was identified by comparing positions, shapes, and relative intensities of the diffraction peaks in powder patterns of the filings to those of standards prepared for this experiment. The d-spacings of the standards were checked against a reference tabulation²⁷ to ensure that they were identified correctly. At least five diffraction peaks were observed for each of the elements or compounds that were found in the ternary systems. The identification of a phase from the positions of the diffraction peaks was unambiguous except for two pairs of compounds, GaSb and AuGa₂ in the Au-Ga-Sb ternary system and InSb and AuIn₂ in the Au-In-Sb system. In both cases, the intermetallic compound and the compound semiconductor had similar crystal structures (fluorite and zinc-blende, respectively) and nearly identical lattice constants. For these cases, a careful comparison of the peak shapes and relative intensities was required to identify the phases. No diffraction peaks were observed that did not correspond to either an elemental species or a known binary compound.

III. Results and Discussion

The results of this investigation are summarized in the ternary phase diagrams shown in Figs.1-4. Each diagram represents an isothermal cut in the range 298K to 873K through a three dimensional plot of the composition of the system as a function of temperature. In general, the phase compositions do not change much with temperature until the first eutectic melts at 621K or so. It must be stressed that these diagrams were constructed for ideal, closed systems in which no vapor phase is allowed to form, so only condensed phases are present. Thus, one is in principle allowed to determine both the temperature and pressure of the system independently. If these two degrees of freedom (f) of the system are specified, then the phase rule states that the number of phases (p) in equilibrium is

$$p = c - f + 2, \quad (1)$$

which for these systems is three, since the number of components (c) or elements in the system is three. Thus, the triangles enclosing the ternary phase diagrams have one of the elements Au, III, and V at each corner. These equilateral triangles are subdivided into smaller triangles, which indicate what three phases may coexist at equilibrium for any particular composition of the system. The elemental composition of any particular system is represented by using the generalized lever rule to locate a point within the triangle defined by Au, III, and V, whereas the relative amounts of the phases that comprise the system are determined by applying the lever rule to the smallest area triangle that contains the composition of system.²⁵

In order to divide the ternary phase diagram into smaller triangles, tie-lines connecting various phases across the diagram must be drawn. These tie-lines define pseudobinary systems, i.e., the two phases connected by a tie-line are in equilibrium with one another and do not react to form products. An additional thermodynamic constraint is placed on the system at a pseudobinary, since it forms the boundary between two three-phase regions; thus $f=3$ and $p=2$. The information presented in the phase diagrams in Fig.1-4 is the identity of the pseudobinary tie-lines contained within each ternary system.

The systems studied in this work are in general somewhat more complex than those studied by Schwartz, et al.,²¹⁻²³ since some of the phases produced in the Au-III-V systems at higher temperatures may have an appreciable solid solubility in one another. This has the effect of making the tie-lines across the ternaries curved, rather than straight, and in some cases makes the tie-lines broader. In the regions of greatest interest, i.e., the compositions closest to the III-V compounds semiconductors, such effects are small and have been ignored, so that all the pseudobinary tie-lines in this work are represented as being straight. A total of 65 different compositions in the four ternary systems were examined, and 25 pseudobinary tie-lines were identified. Eight of these pseudobinaries had been identified previously,^{24,28,29} and one, AuIn-InSb, was found in a system that had been studied and identified as a three-phase region.³⁰ There was no evidence of stable ternary compounds in any of the systems studied. Each of the figures 1-4 contain markers indicating the compositions that were studied in this work. Tables I-IV list the phases actually observed by X-ray powder crystallography for each composition.

In order to map out the ternary systems successfully, it was first important to understand the binary systems that border each ternary phase diagram. The results of previous investigations on the binaries are outlined here as necessary background to discussing the ternaries.

According to the study of Cook and Hume-Rothery,³¹ the maximum solid solubility of gallium in gold (a phase) is 12.4 atom % at 688.5K, 5 % at 473K, and in this study it is estimated to be negligible at room temperature by extrapolation of these data. No solid solution of gold in gallium was detected. There are five solid compound phases in the Au-Ga binary system between room temperature and 764.5K : AuGa_2 ; AuGa ; β, β' phase (nominally Au_7Ga_2), with composition ranging from 20.4 to 23.2 atom % Ga (both β and β' have similar structures with a transition temperature from 648K to 555K); γ, γ' phase (Au_7Ga_3 , Au_2Ga , or Au_9Ga_4), ranging in composition from 29.8 to 31 atom % Ga, with a transition temperature from 559K to 547K; and α_1 phase, ranging in composition from 12.7 to 14.1 atom % Ga, stable only from 621K to 689K. The γ, γ' phase was studied by Puselj and Schubert,³² who prepared this pure phase with initial compositions of Au:Ga :: 70.5:29.5, 70:30, 69.5:30.5, 69:31 and assigned them all to Au_2Ga . In this research, all the Au-Ga compounds were observed to be a silver color except the β, β' and α_1 phases, which were pale yellow.

The Au-In binary system has been investigated by Hiscocks and Hume-Rothery.³³ The solid solubility of In in Au is 12.7% at 963K and 9 atom % at 373K (a phase). No detectable solid solution of Au in In was found. They identified eight intermetallic phases: AuIn_2 ; AuIn , 50.0 to 50.1 atom % In; ψ phase (Au_3In_2), with an appreciable homogeneity range,

stable between 730.6K and 497.4K; γ, γ' phase (Au_9In_4 or Au_7In_3), with a transition temperature from 647.7K to 637.6K, about 30 atom % In; ϵ, ϵ' phase (Au_3In), 24.5 to 25.0 atom % In, which transforms at 612.6K to 572K; ζ phase (Au_7In_2), about 22.2 atom % In; ζ phase; and α_1 phase. The last two phases have a broad composition range. The ψ phase was found to be stable (might be metastable) even at room temperature in the present study. The first four phases are silver-colored, both ϵ, ϵ' and ζ are pink with ϵ, ϵ' being a lighter shade. All the more Au-rich phases are gold-colored.

The Au-As, Au-Sb and the III-V binary systems have been summarized by Hansen,³⁴ Elliott,³⁵ Shunk,³⁶ and Moffatt.³⁷ There is no compound containing Au and As, and these two elements have only a slight mutual solid solubility. The maximum solubility of Sb in Au is 1.12 atom % at 873K, and is almost negligible at room temperature. AuSb_2 is the only stable Au-Sb compound, and is a solid with a melting point at 733K. The mutual solid solubilities between Ga, In and As, Sb are all very small. There are no compounds other than GaAs, InAs, GaSb, and InSb in these III-V binary systems.

For the Au-Ga-As ternary system, pseudobinary tie-lines connected GaAs with four Au-Ga intermetallic compounds and with elemental Au, as shown in Fig.1. These observations differ from those of Panish²⁴, who stated explicitly that both AuGa_2 -GaAs and AuGa-GaAs were pseudobinary systems but apparently considered the Au-GaAs system to be reactive. This is apparently consistent with thin film studies, since gold film reactions with GaAs substrates had been observed in several experiments.¹⁻¹⁷ Thus, this system was examined very carefully to insure that it was indeed

pseudobinary. Three sample compositions, M, G, and L, were chosen along the Au-GaAs composition cut through the phase diagram (Fig.1). Two major solid phases, Au and GaAs, and two minor solid phases, β, β' (β for temperatures higher than 555K and β' for a temperature lower than 648K) and As were identified at all three compositions. The As was sometimes in the form of small pieces separated from the bulk sample. Because of the presence of β, β' and As in the samples studied, the cut connecting them was suspected to be pseudobinary. Composition M was examined using different starting materials. One was a mixture of Au and GaAs, the other was β' phase and As. The products for both sets of starting materials were the same: strong Au and GaAs peaks and very weak As and β, β' phase peaks were observed in the X-ray powder patterns. Based on these results, we concluded that solid Au and GaAs phases form a pseudobinary cut.

The reason As and β' phases appeared was that during the heating process, some of the GaAs decomposed, and vapor phase As separated from the bulk mixture. The composition of the solid sample was then to the left side of the Au-GaAs cut in Fig.1, which is within the tie-triangle bound by Au, GaAs, and β, β' . Had the cooling rate been slow enough, the vapor phase As would have diffused back into the bulk solid and reacted with β, β' to form Au and GaAs according to the equation



Evidently, the cooling rate used was not slow enough, so a small but easily detectable amount of solid As was deposited on the bulk sample and the walls of the capsules, and some β' remained unreacted in the bulk sample.

To test this hypothesis, two more samples at composition L (L1 and L2 in Table I) were placed in fused silica capsules, which were heated and flattened to eliminate the dead space inside them. (The dead space in the capsules used in Panish's experiments was 1 cm^3 , that in our experiments was more than 4 cm^3 , so he found As only in samples containing more than 50 atomic % Au on the Au-GaAs cut, and we obtained As in all samples.) One sample was cooled slowly to room temperature, and the other was quenched at 623K. The phases found in both cases were only Au and GaAs, with no evidence of As and Au-Ga compounds. Panish had also studied the cut between GaAs and 50% Au - 50% As²⁴. In all samples he found GaAs, As, and Au containing a small amount of Ga in solid solution. These findings also support our conclusion, because this cut is in the tie-triangle bounded by Au, GaAs, and As.

The reactions that have been observed between deposited Au films and GaAs substrates¹⁻¹⁷ were driven by the loss of gas phase As in an open system during heat treatment.³⁸ After losing some As, the composition of the solid phases that were initially on the Au-GaAs pseudobinary shifts to the Ga-rich side, where the equilibrium phases are Au, GaAs, and β, β' phase, as identified by Magee,¹ Kumar,¹⁰ Vandenberg,¹¹ Leung,^{13,14} Yoshiie^{15,16} and Zeng.¹⁷ Other Au-Ga phases may also be produced, depending on the heating conditions.¹⁵⁻¹⁷ With the loss of As in an open system, all the Au may be consumed. A series of reactions liberating gas-phase As species are possible, in which the succeeding reaction occurs once the gold containing reactant has been consumed:





For reactions that produce solid phase As, all of these reaction have a positive Gibbs free energy of reaction (ΔG_R), and therefore the reactants are favored. Heating a Au/GaAs system in an As over pressure should prevent any Au-Ga reactions, as observed by Mojzes.^{39,40} Annealing samples with reacted Au films on GaAs substrates in an As ambient should favor the reformation of Au and GaAs, as Miller found.¹² However, if gas-phase As species can form and escape from the system, the reactions will proceed as written in Eqs.3-6 because of the large positive entropy of vaporization of the group V elements.³⁸

The Au-Ga-Sb system proved to be very interesting, and all possible pseudobinary cuts were investigated. Similar to the previous system, both AuGa_2 -GaSb and AuGa-GaSb proved to be pseudobinary. The two cuts connecting β, β' and γ, γ' with AuSb_2 were also pseudobinary. Thus, elemental Au and GaSb are thermodynamically unstable with respect to one another and may react spontaneously in the solid phase, since they cannot be connected by a pseudobinary tie-line (it would cross the β, β' - AuSb_2 and γ, γ' - AuSb_2 tie-lines and thus is not allowed). For the pentagonal region defined by γ, γ' , AuSb_2 , Sb, GaSb and AuGa, all compositions were examined at least twice, using different compounds in the initial sample preparation and cooling from the melt very slowly (cooling time in excess of one week), in order to check the phases. These results indicated that the change in Gibbs free energy (ΔG_R) for the reactions:



was extremely small in magnitude, or the phase separation was kinetically limited, and to obtain the thermodynamically more stable products from the melt would require extremely slow cooling rates. Using the thermodynamic data tabulated in Reference 38, the ΔG_R of reaction for Eq.7 was determined to be -0.44 kcal / mole GaSb at 298K, and 4.69 kcal / mole GaSb at 873K. The absolute value of ΔG_R at 298K is probably smaller than the cumulative uncertainty in the numbers used for the compilation,³⁸ but these results indicate that the existence of a four-phase equilibrium is possible near room temperature in this region of the phase diagram. In principle, such a system is possible only at one particular temperature, where $\Delta G_R=0$. However, in this system, ΔG_R is small in magnitude and does not change drastically with temperature, so there is no strong force to drive the reaction in Eq.7 to completion in one direction or the other. There are no detailed thermodynamic data for the γ, γ' phase to examine Eq.8 but presumably a similar situation exists for this reaction.

The chemical reaction of a gold film deposited on a single crystal GaSb substrate has been characterized by Lince and Williams⁴¹. After heating the sample, AuGa was identified on the sample surface by x-ray microprobe analysis. This sample was also characterized with x-ray diffraction as part of this investigation, and strong Sb, medium AuGa, and weak AuSb_2 peaks were identified. With this result in mind, we tentatively assign AuGa-Sb and AuGa-AuSb₂ as pseudobinary at room temperature (the dashed tie-lines in Fig.2). At higher temperature, the γ, γ' -GaSb cut may be more favorable than AuGa-Sb, but this portion of the Au-Ga-Sb phase diagram is still uncertain.

For the Au-In-As ternary, five Au-In phases, AuIn_2 , AuIn , ψ , γ, γ' , and ϵ, ϵ' , formed pseudobinary cuts with InAs. The ψ phase is not supposed to be stable below 224°C according to Hiscocks and Hume-Rothery,³³ but our reference Au_3In_2 sample was stable at 298K (although it may be a meta-stable state). Standard samples of the ϵ, ϵ' phase composition prepared in this research have powder X-ray patterns that looked like a mixture of ζ_1 and γ, γ' . Because both ζ_1 -InAs and γ, γ' -As were observed to be not pseudobinary, and the phase compositions of O and G in Fig.3 were ϵ, ϵ' , As, and InAs, we concluded that both ϵ, ϵ' -InAs and ϵ, ϵ' -As should be pseudobinary. Thus, Au and InAs may also react spontaneously in the solid state. The α_1 and ζ phases both had broad homogeneity ranges. By the phase rule, the cuts α_1 -As and ζ -As should be pseudobinary, because there are no other possibilities for forming tie-triangles with those compounds in the ternary system. The phases observed for sample P are consistent with this conclusion.

For the case of the Au-In-Sb ternary, eight pseudobinary tie-lines were identified: AuIn_2 -InSb, AuIn -InSb, AuIn -Sb, ψ -AuSb₂, γ, γ' -AuSb₂, ϵ, ϵ' -AuSb₂, ζ_1 -AuSb₂ and α_1 -AuSb₂. A study involving more compositions along the AuIn -Sb cut was carried out by Nikitina and Lobanova (NL),²⁸ who employed DTA, microstructure analysis, and X-ray diffraction to study this system at 18 different compositions. NL observed that AuIn -Sb was pseudobinary and determined the eutectic temperature to be 694K at a composition of 28 atom % Sb. The AuIn -InSb system has also been studied at 20 different compositions by Babitsyna and Luznaya (BL)³⁰ using DTA, optical microscopy, and X-ray diffraction. BL observed three solid phases for this cut, which they identified as InSb, AuIn , and AuIn_2 . It is

possible that a small amount of AuIn_2 was present in the reaction mixture of this study, since Au_{-2} and InSb have peaks in their X-ray crystal patterns at nearly the same values of 2θ . It is also possible that BL observed three phases in their samples because they had not allowed sufficient time for the system to reach equilibrium (recall the situation in the present study for Au-Ga-Sb). If AuIn-InSb is not a pseudobinary cut, $\text{AuIn}_2\text{-Sb}$ should be one, based on the phase rule (Fig.4). Because none of the samples D, C, and E in Fig.4 revealed Sb peaks in X-ray diffraction, AuIn-InSb must be pseudobinary. The ΔG_R for



was calculated to be -0.3 kcal / mole InSb at room temperature, and -0.62 kcal / mole InSb at 873K using the data of Ref.38. This also supports our conclusion that the AuIn-InSb system is thermodynamically more stable than $\text{AuIn}_2\text{-Sb}$. However, this value is also subject to the uncertainty of the data used in the calculations, and with so small a value of ΔG_R , the AuIn_2 and Sb phases could coexist with AuIn and InSb for a long time, since the thermodynamic driving force is not strong for this system.

The Au-In-Sb ternary system has also been studied by Kubiak and Schubert.²⁹ The ternary phase diagram of this study also identified the AuIn-InSb cut as pseudobinary. However, there are some differences between the present phase diagram and that of Ref.29, which identified $\text{AuIn}_{.9}\text{Sb}_{.1}$ as a stable ternary compound and both the $\text{AuIn}_{.9}\text{Sb}_{.1}\text{-AuSb}_2$ and $\text{AuIn}_{.9}\text{Sb}_{.1}\text{-Sb}$ cuts as pseudobinary at 598K . However, when we prepared samples with stoichiometry $\text{AuIn}_{.9}\text{Sb}_{.1}$ (sample T in the Table IV and Fig. IV) in the same manner as described previously, the powder patterns of samples both cooled down to 298K and quenched at 598K clearly revealed AuIn , Sb and

ψ phases. These results indicate $\text{AuIn}_{.9}\text{Sb}_{.1}$ is not a stable compound in the temperature studied here.

The middle tetragonal area of the Au-In-Sb system was not determined unambiguously. The three samples F, I, and J on the $\text{AuIn}-\text{AuSb}_2$ cut and sample Q on the ψ -Sb cut all consisted of at least 3 solid phases, but sample P on the ψ -Sb cut contained Sb and ψ only. Both samples R and U in the tie-triangle bounded by ψ , AuSb_2 , and Sb consisted of ψ , AuSb_2 , and Sb. The ψ -Sb cut was tentatively assumed to be pseudobinary. The α_1 - AuSb_2 and ξ - AuSb_2 cuts should also be pseudobinary, since the products of sample S were α_1 and AuSb_2 and no other possibilities consistent with the phase rule exist.

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V. Conclusion

In this paper, we have shown that elemental gold in contact with the compound semiconductors GaSb, InAs, and InSb in a closed system is thermodynamically unstable with respect to solid phase products. However, Au and GaAs will not react unless gas-phase species are allowed to form. For each semiconductor, at least two Au-III intermetallic compounds are found that did not react with that semiconductor in a closed system. These intermetallic compounds could be used to form thermodynamically more stable contacts to the compound semiconductors, with the AuGa_2 and AuIn_2 intermetallic compounds being the most stable with respect to GaAs, GaSb and InAs, InSb, respectively.

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Table I. Composition of Ternary Mixtures : Au-Ga-As

Sample	Stoichiometry			Phases ^a	
	Au	Ga	As		
A	1	4	2	*	AuGa_2 , GaAs
B	2	5	1		AuGa_2 , GaAs
C	1	3	2	*	AuGa , GaAs
D	2	3	1		AuGa , GaAs
E	7	17	14		γ, γ' , GaAs
F	21	17	8	*	γ, γ' , GaAs
G	1	1	1		Au, GaAs, β, β' (w), As(w)
H	7	16	14		β, β' , GaAs
I	21	16	10	*	β, β' , GaAs
J	3	3	2		GaAs, β, β' , γ, γ'
K	2	3	2		GaAs, γ, γ' , AuGa (w)
L	1	2	2	*	Au, GaAs, β, β' (w), As(w)
L1	1	2	2	298	Au, GaAs
L2	1	2	2	623K	Au, GaAs
M	7	2	2		Au, GaAs, As(w), β, β' (w)
M1	7	2	2		Au, GaAs, As(w), β, β' (w)

^a Determined from X-ray powder patterns. Weak diffraction features are denoted by (w).

* Investigated at both 298K and 873K and found to contain the same phases.

Table II. Composition of Ternary Mixtures : Au-Ga-Sb

Sample	Stoichiometry			Phases ^a	
	Au	Ga	Sb		
A	1	4	2	*	AuGa ₂ , GaSb
B	2	5	1		AuGa ₂ , GaSb
C	1	3	2	*	AuGa, GaSb
D	2	3	1		AuGa, GaSb
E	7	17	14		GaSb, AuSb ₂ (m), AuGa(m), γ, γ' (w), Sb(w)
F	21	17	8	298K	AuGa, GaSb, AuSb ₂ (m), γ, γ' (m)
				873K	GaSb, γ, γ' , AuGa, Sb(m)
G	1	1	1		GaSb, AuGa, Sb, AuSb ₂
H	7	16	14		GaSb, AuSb ₂ (m), AuGa(m), Sb(m)
I	21	16	10		AuGa, GaSb, AuSb ₂ (m), γ, γ' (m), Sb(w)
J	3	2	2		GaSb, Sb, AuSb ₂ (m), AuGa(m), γ, γ' (w)
K	7	3	8		γ, γ' , AuSb ₂ , Sb, AuGa(w)
L	4	1	1	*	β, β' , AuSb ₂
M	21	6	14	*	AuSb ₂ , γ, γ'
N	7	3	3		AuSb ₂ , γ, γ' , AuGa(w), Sb(w)
O	1	1	3	298K	Sb, GaSb, AuSb ₂ (m), AuGa(m)
				873K	Sb, GaSb(m), AuGa(m), Au(w)

^a Determined from X-ray powder patterns. Moderate diffraction features are denoted by (m) and weak features by (w).

* Investigated at both 298K and 873K and found to contain the same phases.

Table III. Composition of Ternary Mixtures : Au-In-As

Sample	Stoichiometry			Phases ^a	
	Au	In	As		
A	1	4	2	*	AuIn_2 , InAs
B	2	5	1		AuIn_2 , InAs
C	1	3	2	*	AuIn , InAs
D	2	3	1		AuIn , InAs
E	7	17	14		γ, γ' , InAs
F	21	17	8	*	γ, γ' , InAs
G	1	1	1		ϵ, ϵ' , InAs, As
H	3	3	1	*	ψ , InAs
I	52	41	7		ψ , InAs
J	7	3	1		InAs, ϵ, ϵ' , As
K	54	32	14		ϵ, ϵ' , InAs
L	3	2	1	*	InAs, ϵ, ϵ' , As(w)
M	7	2	2	*	ξ_1 , As
N	3	1	1	*	ϵ, ϵ' , As
O	50	22	28		ϵ, ϵ' , As, InAs
P	8	1	1		α_1 , As

^a Determined from X-ray powder patterns. Weak diffraction features are denoted by (w).

* Investigated at both 298K and 873K and found to contain the same phases.

Table IV. Composition of Ternary Mixtures : Au-In-Sb

Sample	Stoichiometry			Phases ^a	
	Au	In	Sb		
A	1	4	2	*	AuIn ₂ , InSb
B	2	5	1		AuIn ₂ , InSb
C	1	3	2	*	AuIn, InSb
D	2	3	1		AuIn, InSb
E	7	17	14		InSb, AuIn(m), Sb(w)
F	21	17	8		AuIn, AuSb ₂ (m), Sb(w)
G	1	1	1	*	AuIn, Sb
H	9	3	4	*	γ , γ' , AuSb ₂
I	43	29	28		ψ , Sb, AuIn, AuSb ₂
J	3	2	2	298K	AuIn, ψ , Sb, AuSb ₂
				873K	Sb, ψ , AuIn, AuSb ₂ (m)
K	2	1	1	*	ψ , AuSb ₂
L	4	1	1	*	ζ_1 , AuSb ₂
M	7	2	2	*	ϵ , ϵ' , AuSb ₂ (m)
N	7	3	5		ψ , AuSb ₂
O	4	1	2		ϵ , ϵ' , AuSb ₂
P	6	4	15		Sb, ψ (m)
Q	9	6	2		ψ , AuIn(m), AuSb ₂ (m)
R	30	13	58		Sb, AuSb ₂ (m), ψ (m)
S	17	2	2		α_1 , AuSb ₂
T	10	9	1	298K	AuIn, ψ , Sb(w)
				598K	AuIn, Sb(w), ψ (w)
U	2	1	1	298K	AuSb ₂ , ψ (m), Sb(m)

598K AuSb_2 , $\psi(\text{m})$, $\text{Sb}(\text{m})$

a Determined from X-ray powder patterns. Moderate diffraction features are denoted by (m) and weak by (w).

* Investigated at both 298K and 873K and found to contain the same phases.

Figure Captions

Fig.1 Ternary phase diagram for the Au-Ga-As system at 298K. The broad tie-line connecting γ, γ' and GaAs indicates the range of stoichiometries over which γ, γ' exists. The general features of this diagram are valid for temperatures up to the first eutectic point (about 621K).

Fig.2 Ternary phase diagram for the Au-Ga-Sb system at 298K. The dashed lines indicate tie-lines that are "best guesses", since the X-ray powder patterns revealed mixtures of four or more phases. In this region, the tie-lines may be temperature-dependent (see text).

Fig.3 Ternary phase diagram for the Au-In-As system at 298K and up to the first ternary eutectic point. The broad tie-lines indicate phases with a range of stoichiometries.

Fig.4 Ternary phase diagram for the Au-In-Sb system at 298K and up to the first ternary eutectic point. The dashed line indicates a "best guess" for a tie-line connecting ψ and Sb (see text).

Fig. 1

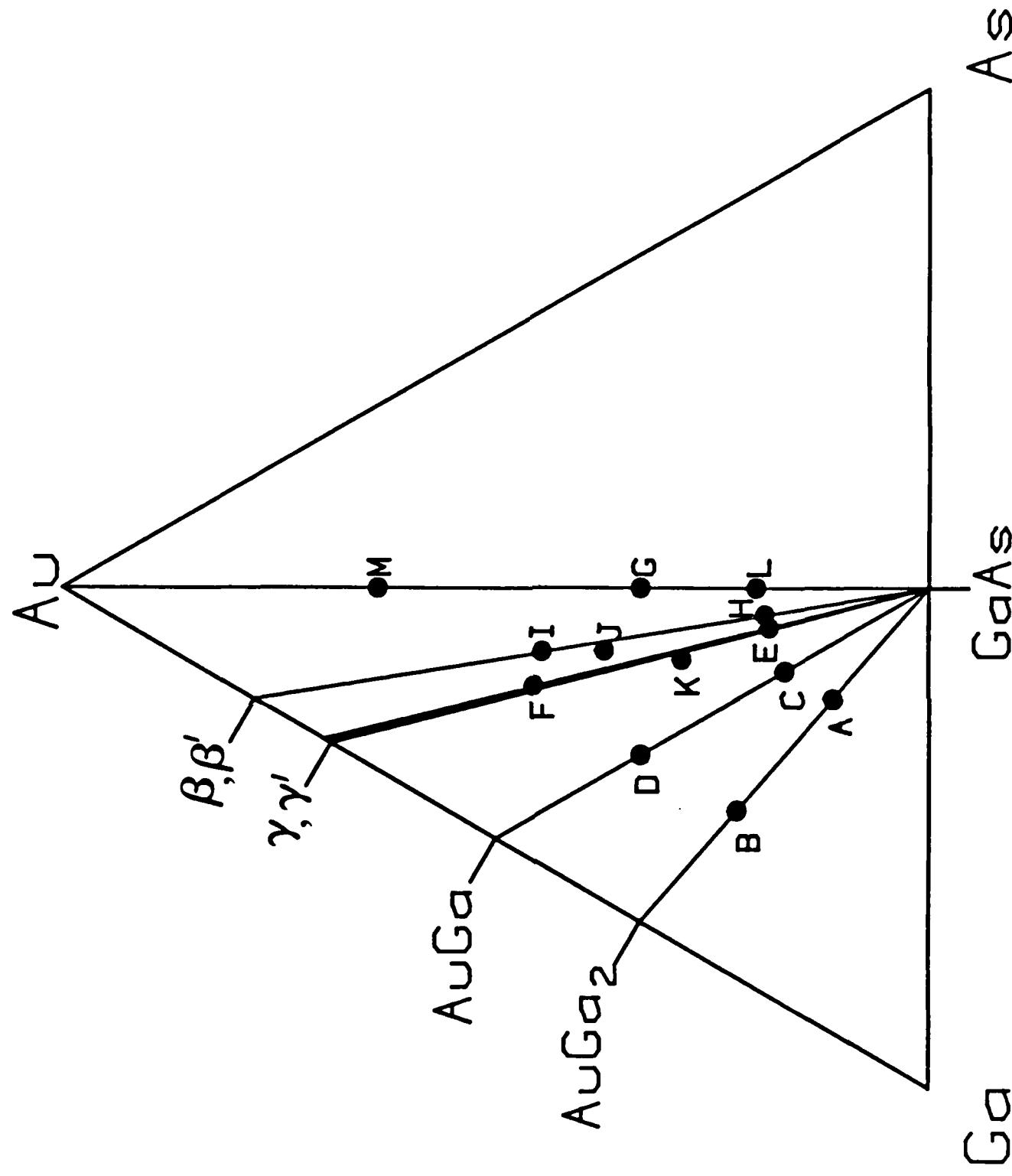


Fig. 2

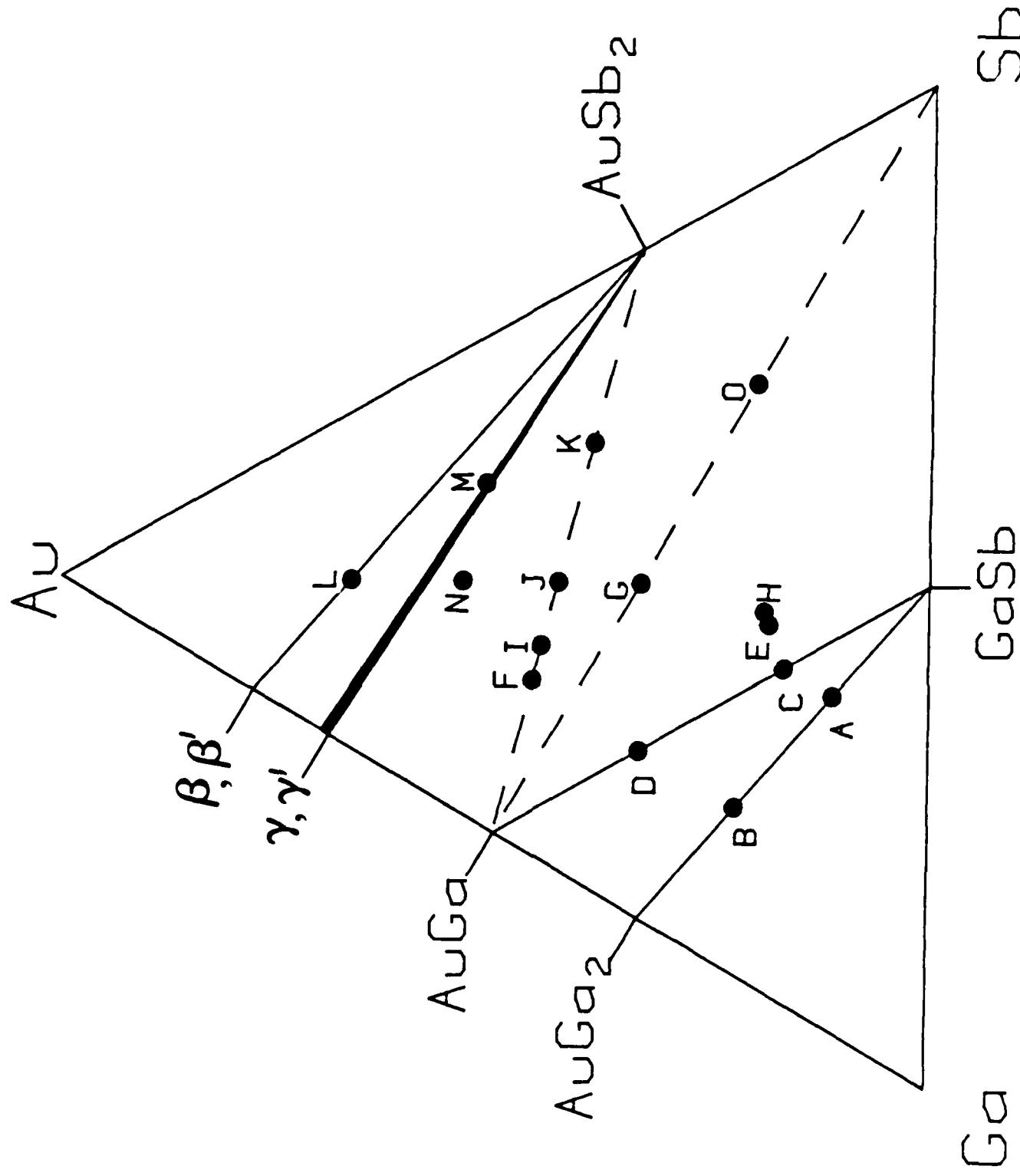


Fig. 3

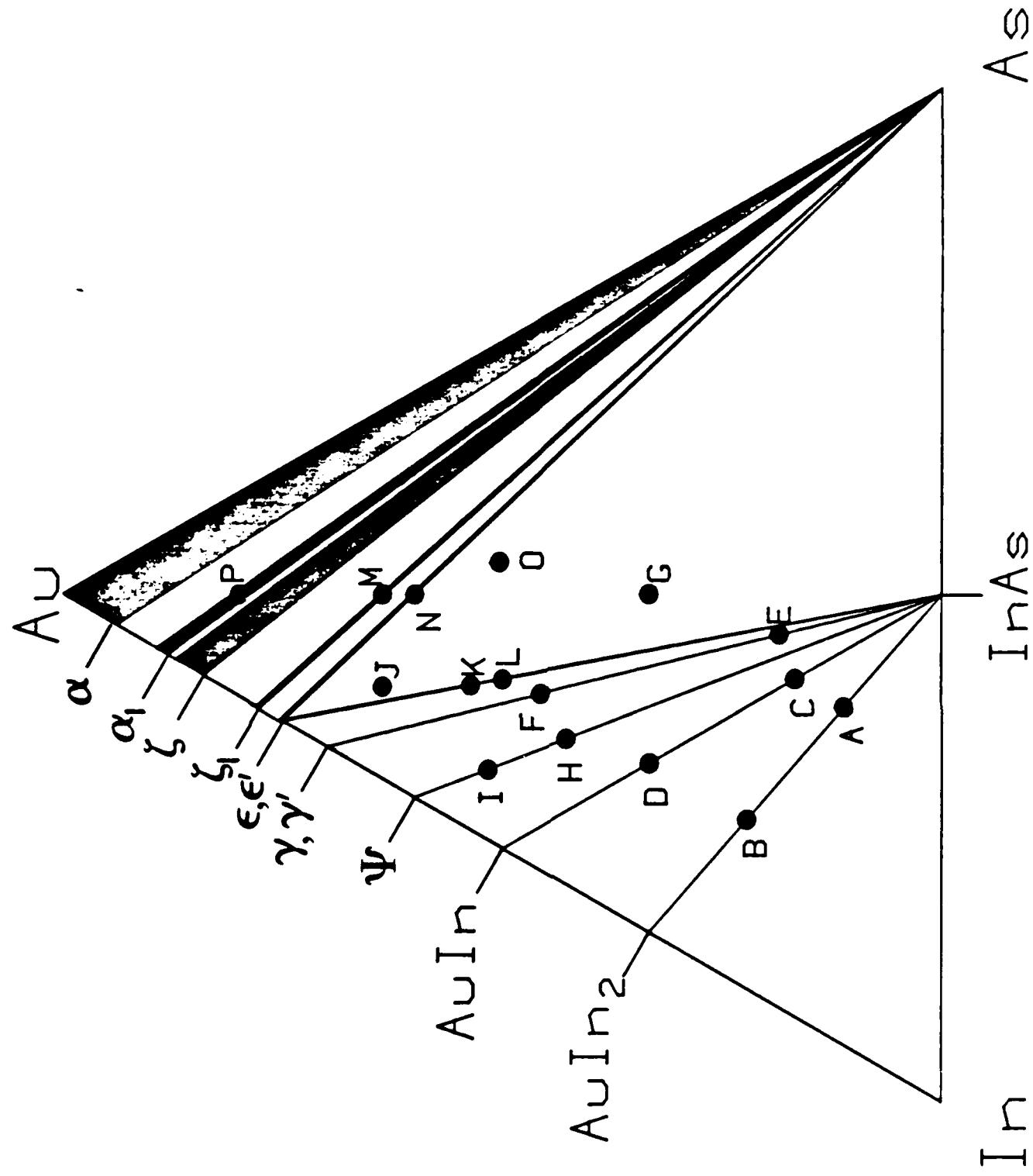
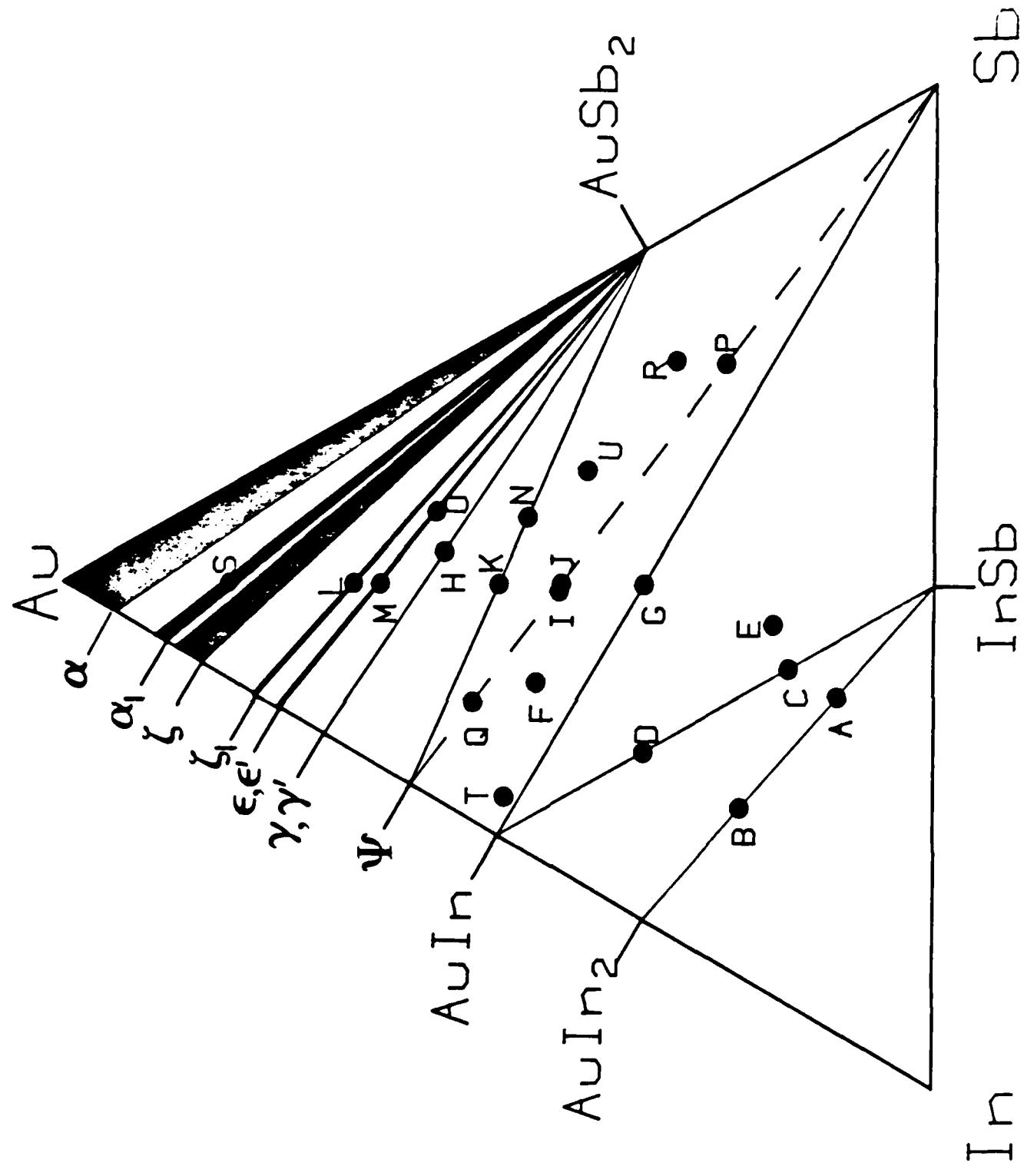


Fig. 4



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